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*Journal of Applied Chemical Research, 16, 4, 65-79 (2022)*

# Application Molecularly Imprinted Solid Phase Extraction Method for Analysis and Determination of Bentazon as a Toxic Herbicide in Water

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*(Received 22 Feb. 2022; Final revision received 08 May 2022)*

**Abstract**

In this paper, a highly selective sample cleanup procedure combining molecular imprinting and solid phase extraction (MI-SPE) was developed for the isolation of toxic bentazon in surface water. The molecularly imprinted polymer (MIP) was prepared using bentazon as the template molecule, methacrylic acid as the functional monomer, and ethylene glycol dimethacrylate as the cross-linking monomer. The bentazon imprinted polymer was used as a selective sorbent for the solid-phase extraction of bentazon from surface water. An offline MI-SPE method followed by high-performance liquid chromatography was also established. To evaluate the applicability of the MIP for separation and determination of bentazon by HPLC, general parameters for SPE including the number of loading solvents, washing solution and eluent, and pH of the sample were optimized following a step-by-step approach. The calibration curve was linear in the range of (0.05 to 0.6 µg $L^{-1}$). The standard deviation of (2.2 %) and detection limit of the method (0.05 µg $L^{-1}$) were obtained for sensor level response. It was shown that recoveries up to approximately 97.0 % from spiked surface water samples could be obtained. It was demonstrated that the proposed MI-SPE-HPLC method could be applied to the direct determination of bentazon in surface water.

**Keywords:** Toxic Bentazon, Molecular imprinting, Solid phase extraction, determination.

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## Introduction

Herbicides are classes of agricultural pesticides for products that improve in quality [1]. Toxic bentazon is the common name for the herbicide 3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one 2, 2-dioxide and is used as a post-emergence herbicide to control broadleaf and sedges in agriculture beans, rice, corn, peanuts, and mint [2,3]. The persistence of pesticides and the fact that their residues remain in food may pose potential health risks to consumers. Therefore, to ensure food safety and environmental protection, research needs to focus on the proper use of pesticides in terms of licensing, registration, and compliance with the maximum residual limit (MRL). For this purpose, field loss studies on the persistence of pesticides in food and the behavior of pesticide residues in water samples are required [4,5]. However, due to the complexity of environmental and biological samples as well as the importance of determining ultra-low levels of analytes, a selective and sensitive sample preparation step before detection is required when using mentioned analytical methods [6]. A common approach for sample preparation, which has become a candidate of choice in many analytical fields for handling and analysis of complex samples [7], is solid phase extraction (SPE).

SPE has been designed for the concentration and clean-up of samples, as well as for the removal of toxic or valuable substances from a variety of predominantly aqueous solutions [8]. SPE compared to liquid-liquid extraction (with relatively clean extractions) has many benefits such as being is: cheap, quite fast, less hazardous and expensive solvents requirements, having good recovery potential, and being automatic can be automated [9]. Our previous works reported the successful use of SPE for sample preparation of some compounds [10]. Most SPEs are based on the adsorption of analytes on a solid phase. The solid phase is then washed from interference compounds and the analytes of interest are desorbed by elution using a liquid. Sorbents for SPE are divided into three groups including inorganic oxides, low-specificity sorbents, and compound-specific and class-specific sorbents [11].

In the last decades, due to insufficient selectivity of inorganic oxides and low specific sorbents, a growing trend has been focused on the last sorbents. Immunosorbents and molecularly imprinted polymers (MIP) are the commonly used compound-specific and class-specific sorbents. Although immunosorbents show high selectivity to target molecules, they are less stable, difficult to prepare, and expensive, so their usage is reduced [12]. Recently, because of stability, low cost, and ease of preparation, MIPs have become an interesting research field for the preparation of specific sorbents for SPE of compounds in environmental and occupational samples [13]. It should be mentioned that usage of MIPs in SPE is a hopeful and novel method of development in analytical chemistry [14]. MIPs are artificial polymers with recognition binding sites able to bind a molecule or its structural

analogs from a complex sample [15,16]. The polymers are formed by the polymerization of functional monomers and a cross-linker in a complementary shape around a template molecule. Template extraction will allow recognition binding sites to remain in the polymer matrix. The application of MIPs as sorbents in solid phase extraction, namely molecularly imprinted solid phase extraction (MISPE), has been successfully reported for many compounds. Some of them are; atrazine [17], nitrophenol [18], Carboxin [19], propiconazole in wheat and soil [20], and identification of the phenolic profile of fruits of Lycium barbarum [21]. The polymers are framed by the polymerization of utilitarian monomers and a cross-linker in an integral shape around a template atom. Template extraction will permit acknowledgment-restricting destinations to stay in the polymer network [22]. The point of this work was to integrate toxic bentazon engraved polymers for utilization as dissolvable in the SPE cartridge. At that point, the MISPE system for extraction of the following measure of toxic bentazon in surface water was created and its consequent and its HPLC examination were advanced.

## Experimental

*Reagents and materials*

Analytical grade bentazon was purchased from Sigma-Aldrich. Acetonitrile, methanol, ethanol, chloroform, and acetic acid were purchased from Merck and were analytical or HPLC grade. Methacrylic acid (MAA) (98%) as the functional monomer, ethylene glycol dimethacrylate (EDMA) (98%) as the cross-linker, and α,α′-Azoisobutyronitrile (AIBN) (98%) were purchased from Merck (Hohenbrunn, Germany). MAA was distilled under a vacuum to remove the inhibitor prior to polymerization. To clean the inhibitor from EDMA, it was washed with 10% aqueous sodium hydroxide three times, followed by washing with pure water, and then dried over anhydrous sodium sulfate. Toxic bentazon standard solutions were prepared by dilution of the stock solution (5 μg/L in methanol) with LC-grade water.

*Instruments*

For analyzing toxic bentazon, high-performance liquid chromatography (Agilent Technology 1200 series) was used. The instrument was equipped with a CO-2060 column oven, Bin pump sl De 63060570, and Tcc sl de 64156237 Dad detector. The detector was set at 254 nm. The chromatographic column was $C_{18}$ (250×4.6 mm i.d.; Supelco, USA). The mobile phase was a mixture of acetonitrile, methanol, and water (60:20:20) containing 5 μL $H_3PO_4$ at a flow rate of 1 mL/min. The column temperature was fixed at 40C°. The injection volume was 10 μL.

*Preparation of the imprinted polymer*

For the preparation of the bentazon-imprinted polymer, the template (bentazon, 0.072 g, 0.3 mmol) was dissolved in the porogen (chloroform, 15 ml) in a 25 ml thick-walled glass tube. The functional monomer (MAA, 0.15 mL, 1.80 mmol), the crosslinking monomer (EGDMA, 1.1 mL, 6. 0 mmol), and the initiator (AIBN, 0.08 g, 0.51 mmol) were then added. The resultant solution was cooled on an ice bath and degassed with oxygen-free nitrogen for 5 min before being sealed under nitrogen. The polymerization was allowed to proceed at 60 C° for 24 h in a water bath. After this period, the glass tube was broken and the monolith obtained was ground mechanically and wet sieved using acetone to obtain regularly sized particles with diameters between 25 μm and 50μm suitable for the MISPE evaluations. A non-imprinted polymer (NMIP) was prepared and treated identically to the MIP, the only difference being that there was no bentazon present during polymerization [23,24].

*Procedure of SPE*

For the sensitive and quantitative determination of toxic bentazon at the required levels, an SPE procedure was carried out using this imprinted polymer as an enrichment sorbent. Polymer particles with a size between 25 and 50 μm were separated and collected by a steel sieve. Small columns with a length of 53 mm and an inner diameter of 6.5 mm were filled with 100 mg of molecular mold polymer and molecular non-mold polymer. SPE cartridges were preconditioned with 2 mL of ultra-pure water and 2 mL of methanol to activate the sorbent before the enrichment procedure. 8 mL of toxic bentazon solution was uploaded onto the preconditioned cartridge. After loading, the vacuum was still applied to the cartridges for 5 min to remove the residual solvent. Eluting step was performed using 2 mL of methanol/acetic acid (9/1, v/v) mixture solution [25,26].

*MISPE procedure of spiked surface water*

The performance of the optimized MISPE procedure was evaluated for trace analysis of bentazon in surface water. Surface water was collected from farmland and its pH was adjusted to 10 with 20% aqueous NaOH (optimized pH obtained in this study). The surface water was filtered to remove particulates and spiked with bentazon at 1, 50, 100, and 200 μg $L^{-1}$. Then, MISPE of 500 mL of 1 μg $L^{-1}$ (sample loading flow rate: 1.5 mL/min) and as well as 20 mL of 50, 100, and 200 μg $L^{-1}$ (sample loading flow rate: 1 mL/min) were carried out.

## Results and Discussion

*FTIR analysis*

The Spectra of bentazon molecular mold polymers and molecular non-mold polymers prepared by bulk polymerization are shown in (Figure 1). As it turns out, the spectra of both polymers are structurally similar. In the tensile vibration spectrum, the tensile vibration 3500 $cm^{-1}$ of the carbonyl group 1730 $cm^{-1}$, C=O tensile vibration 1260 $cm^{-1,}$ and C-H flexural vibration 765, 1390, 1460, 2956 $cm^{-1}$ were observed in the regions. The results of evaluation and comparison of both spectra show that the adsorption attributed to the C-H tensile vibration (2956 $cm^{-1}$) of the methylene group, the tensile vibration (1730 $cm^{-1}$) of the carbonyl group, the tensile vibration (1260 $cm^{-1}$) of C-O and the C-H flexural vibration (1460 $cm^{-1}$) of $CH_2$ (2956 $cm^{-1}$) are relatively stronger for molecular mold polymers than for molecular non-molecular polymers. In non-molecular form polymers, some carboxylic acid groups of monomers may be converted to carboxylic acid dimers during the polymerization reaction, so that free carboxylic acid groups in molecular non-form polymers are less than molecular form polymers. In the molecular form polymer, the carboxylic acid groups of the monomeric acid are linked together by hydrogen bond interactions with the NH and C=O groups of the bentazon molecule during the polymerization process [24,25].

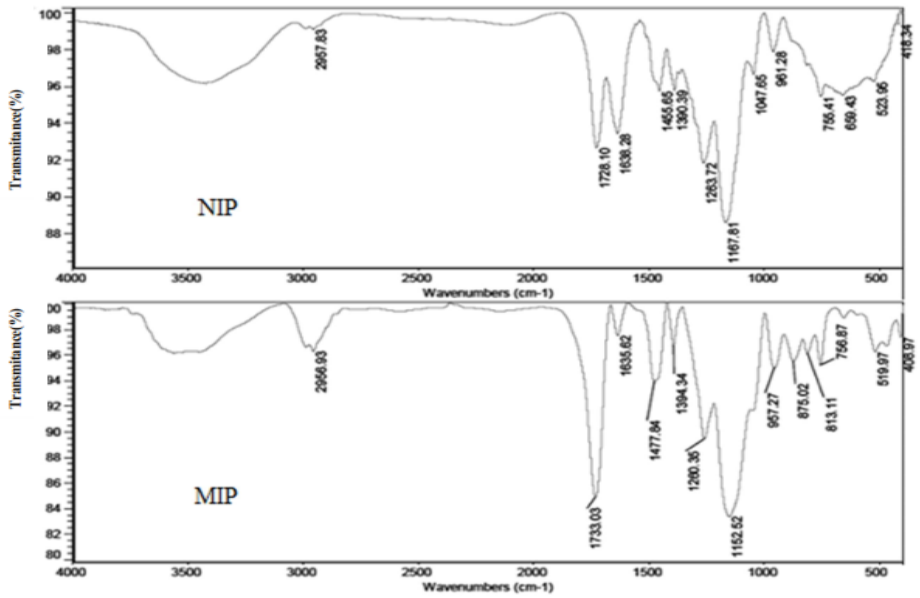


**Figure 1.** The FT-IR transmittance spectrum image for toxic bentazon on MIPSE and NISPE.

*Preparation conditions of molecularly imprinted polymer*

The molar proportion of template/monomer/cross-linker is one of the essential parameters that influenced the capacity of MIP orchestrated in the combination procedure. The main fitting molar ratio of template /monomer can bear the cost of high selectivity with MIP. What's more, the measure of cross-linker ought to be sufficiently high to keep up the steadiness of the acknowledgment destinations [27]. Through complex enhancement explores, the MIP synthesized at the molar

proportion of 1:6:20 (template/monomer/cross-linker) in 15 ml of chloroform demonstrated a superior fondness and selectivity and were picked as synthetically states of bentazon-MIP. Different concentrations of bentazon in the range (0.05–0.6 µg $L^{-1}$) at the same volume (50 ml) were passed through the column for measuring retention capacity. The retention capacity (mg adsorbed bentazon/g of Sorbent) was gotten to be 12.6 $mgg^{-1}$. The enrichment factor as an essential parameter on the preconcentration step was controlled by passing 100 ml of the bentazon arrangement with the convergence of 0.5 µg $L^{-1}$ through the MIP section. After analyst elution with 2 ml of methanol-acetic acid solution with a ratio of 1:9 (V/V) was used and the amount of analyte was measured by HPLC. (Equation. 1), was used to calculate the recovery percentage. In this regard, CB is the amount of recovered concentration, CA is the initial concentration, VB is the volume of the recovered solution and VA is the volume of the initial solution [27,28].

$$\text{Recovery} = \frac{C_B \times V_B}{C_A \times V_A} \times 100 \qquad (1)$$

Adsorption capacity is an important factor that determines how many analytes the adsorbent can absorb. To calculate the adsorption capacity, 500 ml of 0.5 µg $L^{-1}$ solution was passed through a column containing adsorbent. Using the resulting solution concentration and initial concentration and according to (Equation. 2), the amount of analyte adsorption by polymer (Tb) was calculated. In this regard, V is the volume of the initial solution (ml), Ci is the concentration of the initial solution (µg/ml) and Cf (µg/ml) is the concentration of the solution after adsorption [28,29].

$$(\mu g) = V(C_i - C_f)\ \ Tb \qquad (2)$$

The amount of analyte adsorption per gram of polymer was calculated using Equation (3).

$$C_{MIP}\ (\frac{\mu g}{g}) = T_b/m \qquad (3)$$

The molecular molding factor (IF) was also used to evaluate the effects of molding. The molecular molding factor was calculated according to (Equation. 4). In this regard, $C_{MIP}$ and $C_{NIP}$ indicate the amount of analyte adsorption per gram of mold and non-mold polymers, respectively [28,29].

$$IF = C_{MIP} - C_{NIP} \qquad (4)$$

*Optimization of extraction conditions*

To reach the highest extraction efficiency, factors influencing the extraction were investigated and optimized as follows:

*Optimization of SPE procedure*

In order to evaluate the applicability of the MIP for separation and determination of bentazon by HPLC, general parameters for SPE including the number of loading solvents, washing solution and eluent, and pH were optimized following a step-by-step approach. Different volume (2 mL, 4 mL, 6 mL, 8 mL and 10 mL) of bentazon solution (0.5 μg $L^{-1}$) was loaded onto the cartridges that contained 100 mg MIP of bentazon. According to the compared data obtained under the same condition, 8 mL of bentazon solution (0.5 μg $L^{-1}$) was selected as the sample loading condition in subsequent experiments.

*Effect Type of eluting and volume eluting solvent*

The washing step was a crucial procedure to maximize the specific interactions between the analytes and binding sites and to simultaneously decrease non-specific interactions to discard matrix components of the polymer. In this part, ethanol–$H_2O$ solution of different ratios (19:1, 9:1, 8:2, 7:3, and 5:5, v/v) and different volumes (1 mL, 2 mL, 3 mL) was investigated on the MIP and NMIP cartridges (Figure 2).

When 1 mL washing mixture of ethanol and $H_2O$ was at the ratio 19:1 and 9:1, no obvious effect was caused on the retention of bentazon on the sorbent with the recoveries being (MIP: 91.3% and 92.4%, NMIP: 69.2% and 66.2%). With the increase of $H_2O$ in the 1 mL washing solution (8:2), the recovery from the NMIP sorbent was decreased rapidly to (53.7%), while the recovery from the MIP sorbent was not reduced (92.2%). In other words, the ethanol-$H_2O$ solution (8:2) could decrease non-specific interactions, but do not affect the interaction between the analyte and binding sites. However, the higher portion of $H_2O$ (7:3 and 5:5) led to the large decrease of the analyte on both MIP (56.6% and 46.5%) and NMIP sorbent (48.7% and 36.5%). That might result from the disruption of specific interactions between the analyte and binding sites caused by the changed polarity of washing solution.

The recoveries on MIP and NMIP column were in small difference when using ethanol–$H_2O$ at the ratio of 7:3 and 5:5 as the washing solution. It was because that the MIP and NMIP sorbent held similar specific surface areas, which could bring about similar non-specific interaction to the analyte. By comparison of the obtained data of different washing volumes, the results showed that the recovery of MIP with 1 mL ethanol–$H_2O$ solution (8:2) (92.2%) was almost equal to that with 2 mL washing solution (93.1%), but higher than that with 3 mL (85.1%) as the washing condition. Based on the results above, 1.5mL ethanol–$H_2O$ solution (8:2) was chosen as the washing condition in further research [30,31].

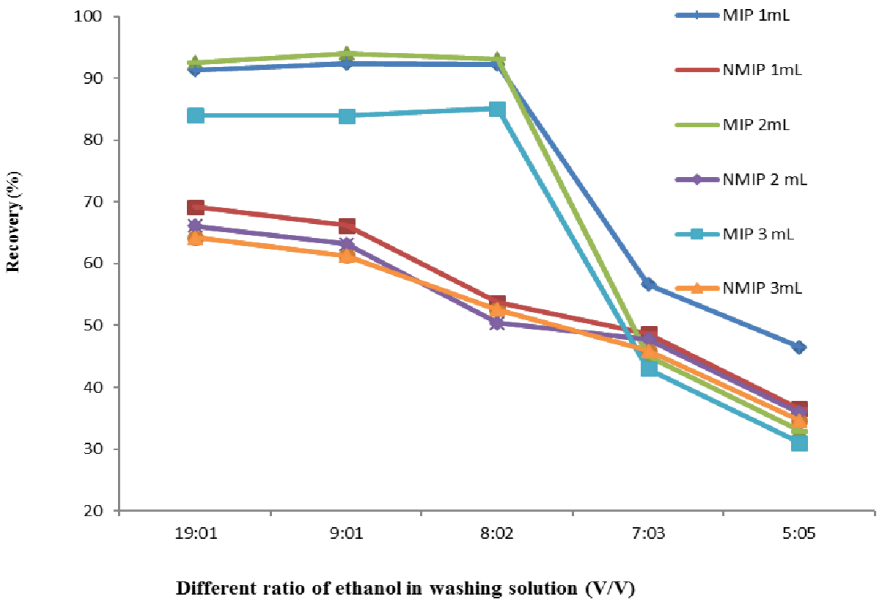


**Figure 2.** Recoveries of toxic bentazon on MIP and NMIP column with different washing solutions.

*Effect of pH*

The effect of pH on the sorption of bentazon was investigated by varying the solution pH from 1.5 to 10.0. Several experiments were performed by equilibrating 100 mg of the imprinted particles with 8 mL of solutions containing 50 ng/mL of bentazon under the desired range of pH. The pH dependence of extracted percentage of bentazon is shown in (Fig. 3). As seen, the binding of bentazon increased with increasing pH and reached a maximum at pH of 8.5–10.0. At low pHs, the nitrogen hetero-atoms can be protonated and, therefore, negligible amounts of bentazon are adsorbed to the polymer [32].

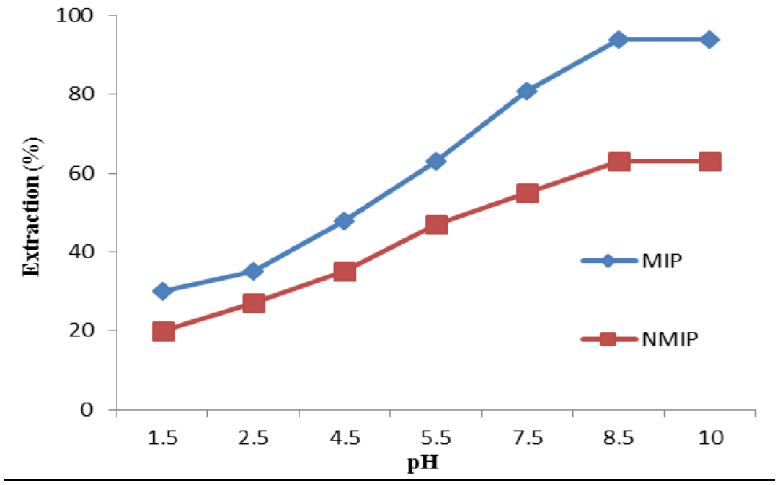


**Figure 3.** Impact of pH on the sorption of toxic bentazon on imprinted polymer particles.

*Effect Type of eluting solvent*

An appropriate eluent should be chosen to ensure the analyte can be completely eluted from the MIP cartridge. For this purpose, different types of solvents including $H_2O$, methanol, $H_2O$/methanol (9:1, 7:3, and 5:5, v/v), methanol/acetic acid (9:1, 7:3 and 5:5, v/v), ethanol/acetic acid (9:1, 7:3 and 5:5, v/v), were applied and compared for the selection of the final eluent. Among the tested solvents, acetic acid-containing eluent offered a higher recovery than other types of solvents, and in the case of methanol/acetic acid (9:1) as the eluent, the highest recovery was achieved (more than 94%). The solvents containing methanol and $H_2O$ could almost achieve the same recovery (70–80%). These results proved that the acidity of the eluent is of more importance than the polarity in the desorption procedure between the template molecule and the MIP [31,33].

*Effect of volume of the eluting solvent*

The eluent volume is also a crucial parameter to be optimized in SPE. The chosen volume of eluent must be just sufficient to elute the analyte from the sorbent. Thus, recoveries of bentazon were studied by applying different eluent volumes of 1–5 mL. The results indicated that good recoveries were achieved at 2 mL of methanol/acetic acid (9:1), and more volume provided similar recovery values, which showed that 2 mL of methanol/acetic acid (9:1) was enough to provide a quantitative elution of the analyte from the sorbent (Figure 4).

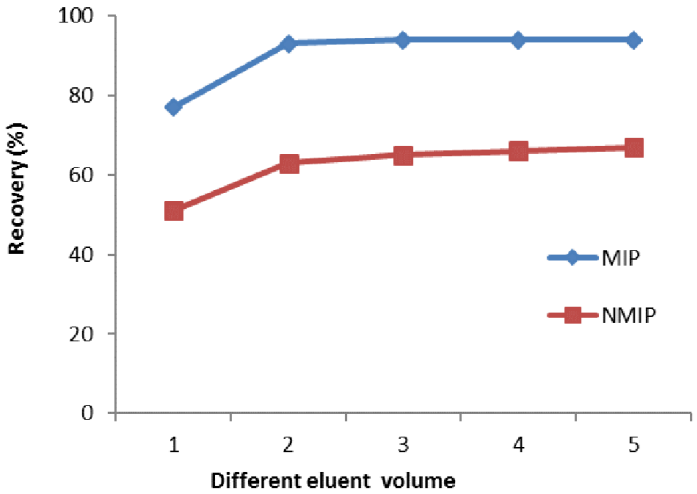


**Figure 4.** Recoveries of toxic bentazon in SPE procedure with different eluent volumes.

*Salting out effect*

The effect of salt on the extraction efficiency was evaluated by adding enough solid NaCl to the solution to have a concentration of 0.1 to 2.0 M of NaCl in a sample solution. In the presence of 2.0

M of NaCl, highest recovery of the analyte was obtained. However, there was no further improvement at higher concentrations of salt.

*Calibration graph and reproducibility*

In this paper, after optimizing the factors affecting a series of standards in the range (0.05–1.0 µg $L^{-1}$) of toxic bentazon was prepared in methanol and used to determine the analytical parameters. The response of HPLC schemed against the concentration of this compound (Fig. 5) and the calibration curve equation was built up by the least-squares method. The linear dynamic range for the toxic bentazon determination was (0.05–0.6 µg$L^{-1}$). The detection limit was (0.05 µg$L^{-1}$) and the relative standard deviation of toxic bentazon was (2.2%) as shown in (Figure 5) [17,33,34].

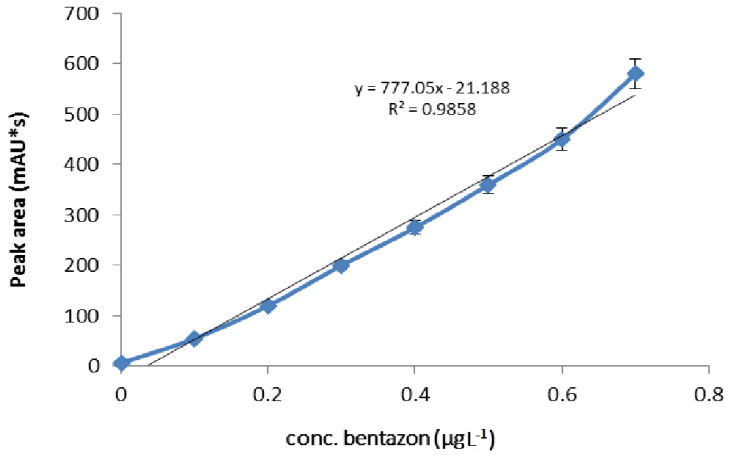


**Figure 5.** The calibration graph for toxic bentazon the response of HPLC was schemed against.

*Analytical performances and method validation of the developed method*

The analytical performance of the suggested pipette-tip extraction coupled with HPLC was evaluated, and the results are summarized in (Table 1).

**Table 1.** Analytical figures of merit for pipette-tip extraction of toxic bentazon.

| Parameter | Analytical feature |
|---|---|
| Dynamic range (M) | (0.05 - 0.6 µg $L^{-1}$) |
| $R^2$ (determination coefficient) | (0.9858) |
| pH | (8.5) |
| The detection limit ( µg $L^{-1}$) | (0.05 µg $L^{-1}$) |
| Relative Standard Deviation (RSD) | (2.2 %) |
| Advantages | High repeatability, Sensitivity, Selectivity, Wide linear range. |

[a]LOD, was based on $3S_b/m$ criterion for 10 blank measurements; RSD, relative standard deviation, for 5 replicate measurements of 0.5 µg $L^{-1}$ of each analyte Limit of detection (LOD) was obtained based on a signal-to-noise ratio of 3. The linearity range was studied by varying the concentration of the standard solution from (0.05 to 0.6 µg $L^{-1}$).

*Preparation of MIPs*

The preparation procedures for MIPs of toxic bentazon were described in (Figure 6). The functional monomer initially formed complexes with the template molecules. Then, their functional groups were held in position by the highly cross-linked polymeric structure after polymerization [35]. The MIPs were finally grafted onto the surface of the Methacrylic acid (MAA) as the functional monomer, ethylene glycol dimethacrylate (EDMA). After template removal, specific binding sites were left in the polymer material.

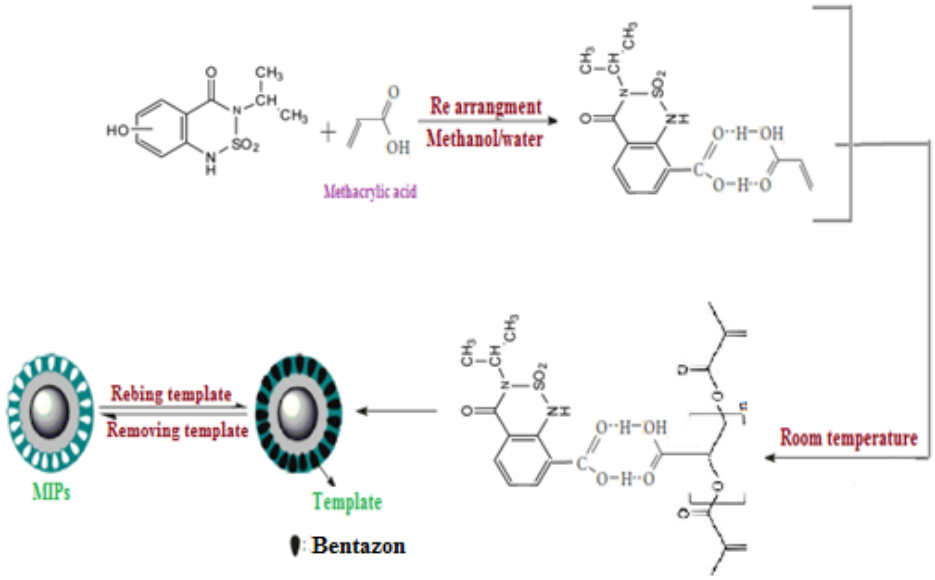


**Figure 6.** Process for preparing MIPs of toxic bentazon.

*Real Sample Analysis*

To evaluate the efficiency of the proposed MISPE procedure for trace analysis of toxic bentazon to the final concentration of the sample volume 500 mL (0.5, 1.0, and 1.5 (μg $L^{-1}$), according to the instructions mentioned for toxic bentazon experiment 3, replicates measuring section [36,37]. The obtained percentage percentiles in (Table 2), indicate that the prepared MISPE has a very good performance for the extraction of bentazon in water samples. Therefore, the determination of bentazon in samples was confirmed utilizing the standard addition method. The level of the bentazon was estimated to be below the detection limit of the related element. Based on the outcomes of replicating analyses for each sample, it was shown that the bentazon retrievals were mainly quantitative with a low RSD. The potentiality of the recommended method for the separation of trace quantities of these elements in distinct samples was proven.

**Table 2.** The percentage recovery of bentazon on MISPE and NISPE of surface water spiked with toxic bentazon, (n=3).

| Analyte concentration (µg $L^{-1}$) | 1 | 50 | 100 | 200 |
|---|---|---|---|---|
| Recovery on MISPE | 91.2±2.4 | 92.3±3.6 | 92.8±1.5 | 94.1±2.6 |
| Recovery on NISPE | N.D. | N.D. | 52.6±1.8 | 65.5±2.3 |

N.D: Bentazon was not detected in the elution solvent

*Pipette-tip solid phase extraction*

Pipette-tip solid phase extraction based on bulk polymerization for the separation and preconcentration of bentazon followed by high-performance liquid chromatography has been developed for the extraction of bentazon in water samples. Due to very high surface areas and short diffusion rate, high adsorption capacities can obtain in a very short time. The optimized method is found to be fast, economical, sensitive, accurate, and simple shown in (Figure 7) [17,38].

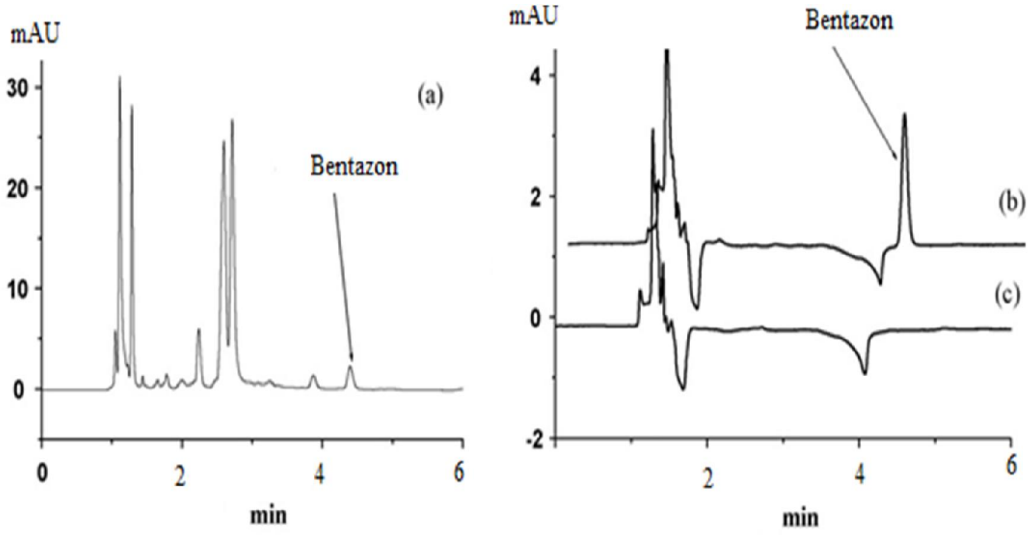


**Figure 7.** HPLC chromatograms were obtained from the extraction of (a) water sample spiked by (0.5 µg $L^{-1}$) of toxic bentazon (b) After extraction of toxic bentazon with MISPE (c) After extraction of toxic bentazon with NISPE.

*Comparison of this method with other methods*

A comparison of the proposed method with the other previously reported methods demonstrates the feasibility of the PT-SPE-HPLC method and its reliability for the analysis of bentazon (Table 3). The LOD and LDR in this work are comparable to and lower than some studies. The standard deviation (RSD) is better than some and comparable with those of the other studies. It can be concluded that PT-SPE-HPLC is a sensitive method that can be used for the ultra preconcentration and extraction of bentazon from environmental samples.

**Table 3.** Comparisons of the proposed method with other methods for extraction of toxic bentazon.

| Model | LOD (µg $L^{-1}$) | LDR (µg $L^{-1}$) | RSD (%) | References |
|---|---|---|---|---|
| Fluorescences | 0.5 | 0.05-200.0 | 3.0 | [3] |
| SPME | 0.3 | 1.0-50.0 | 5.0-8.0 | [38] |
| MWCNTs/SPE | 14-19 | 0.003-10.0 | 7.2 | [39] |
| Cyclic Voltammetry | 1.6 | 10.0 -80.0 | 3.4 | [40] |
| $ZnFe_2O_4$ NPs/ reduced graphene oxide /CPE | 0.07 | 0.1-20.0 | 3.25 | [41] |
| PT/SPE | 0.03 | 0.05-100.0 | 3.78 | [42] |
| PT/SPE | 0.001 | 0.05-0.6 | 3.2 | This work |

[a]LDR, linear dynamic range is the minimum detectable concentration and the largest concentration that the response factor falls outside.

## Conclusion

In this paper, a determination of toxic bentazon was set up by bulk polymerization utilizing MAA and EGDMA as the useful monomer and cross-linker individually. Through evaluation in a series of adsorption experiments, the polymer exhibited good recognition and selective ability, suggesting that it could be a useful tool for analytical purposes. Furthermore, a method was successfully developed to detect bentazon at low concentration levels in surface water using this MIP as an enrichment sorbent of pipette-tip solid phase extraction coupled with high-performance liquid chromatography. It should focus on the bentazon determination in other samples in further research. The lowest determining error bentazon could be obtained in a short time, which strongly confirms the greater contribution for the deletion of bentazon by bulk polymerization of SPE coupled with HPLC. This paper also offered a new method to determine other analytes in different samples.

## Acknowledgments

The authors would like to acknowledge that the research was partially supported by the Islamic Azad University, Branch of Kerman, Iran.

## Disclosure statement

No potential conflict of interest was reported by the author(s).

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